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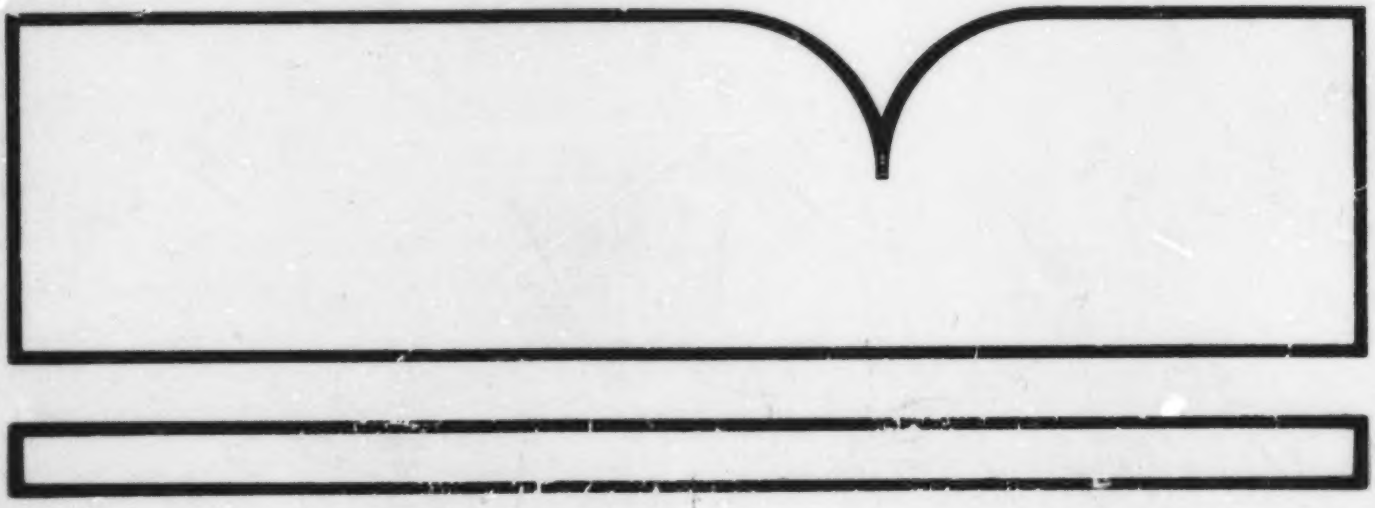

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16. ABSTRACT
This research brief is a summary of the extensive review and critical analysis of the literature on products of atmospheric photochemical reactions in the lower troposphere, and an assessment of that body of research information. The review is reported separately (Measurements of the Products of Atmospheric Reactions in Laboratory Studies and in Ambient Air - Relationships Between Ozone and Other Products: A Review submitted to Atmospheric Environment). The conclusions reached are as follows: (1) The products other than ozone and nitrogen dioxide in combination occur in ambient air at concentrations approaching or equalling the concentrations of ozone;(2) the other products show the same directional characteristics as ozone in ambient air; (3) the quantitative relationships between these other products and ozone are complex and are different for each product;and (4) the quantitative relationships between these products and precursor hydrocarbons and nitrogen oxides are complex and are different for each product.

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ENVIRONMENTAL RESEARCH BRIEF

An Assessment of Ozone as a Surrogate for Other Products of Atmospheric Photochemical Reactions

A. P. Altshuller

In addition to ozone and nitrogen dioxide, many other gaseous and aerosol products of atmospheric photochemical reactions occur alone or in combination at significant concentration levels compared to ozone in urban areas. The more abundant of these other products include formaldehyde, nitric acid, peroxyacetyl nitrate and sulfate. Aldehydes are the most abundant group of such products. At the time of maximum ozone concentration, these other products in combination can constitute about half of the ozone concentration in the South Coast Air Basin of California. On a 24-hour average basis, these products in combination can equal or exceed the ozone concentration in urban areas.

Ozone should serve directionally as a satisfactory surrogate for these other products of atmospheric photochemical reaction in the ambient atmosphere. However, laboratory studies do indicate some circumstances in which ozone may not be an adequate surrogate directionally. In addition, both ambient air measurements and laboratory results indicate that complex quantitative relationships exist between ozone and other products, and between these products and the precursor hydrocarbons and nitrogen oxides.

Monitoring for aldehydes and peroxyacetyl nitrate has been carried out at locations in the South Coast Air Basin and in New Jersey. It appears practical to carry out monitoring efforts for products other than ozone if necessary in a limited number of critical urban areas.

Introduction

This assessment is intended as an evaluation of how well ozone measurements can serve as a surrogate for the variations in the concentrations of other products of atmospheric photochemical reactions in the ambient air. This work was done as a result of a request from staff in the Office of Air Quality Planning and Standards to the Office of Research and Development. This assessment is one of a group of four assessments requested concerned with the following topics: (1) natural sources of ozone, (2) transport and reactions of ozone, and (3) products of photochemical atmospheric reactions.

A scientific review has been prepared considering in detail the other products of atmospheric photochemical reactions as they relate to ozone. The mechanisms of formation, types of products identified in laboratory studies, and the ambient air concentrations and distributions are discussed in this review. Because nitrogen dioxide has received much scientific consideration and assessment elsewhere, nitrogen dioxide is not considered in detail within the review.

Qualitative Summary of Results of Studies

A substantial number of inorganic and organic products of photochemical atmospheric reactions have been identified and measured in laboratory studies. Many of these products are gases or vapors, while others occur as aerosols in the atmosphere. While several of these products along with ozone are "oxidants," most of the products do not respond as oxidants to the measurement methods used in the laboratory and ambient air.

More products have been identified in laboratory investigations than in the ambient air. Therefore, the lack of identification in the ambient atmosphere of products observed in the laboratory does not necessarily imply that these products are not present in ambient air. Even in

laboratory studies carbon and nitrogen balances between reactants and products often are difficult to obtain. Therefore, additional products not yet identified even in the laboratory may be present in the ambient air.

The inorganic products of atmospheric photochemical reactions identified in laboratory and/or ambient air include carbon monoxide, carbon dioxide, nitrogen dioxide, nitrogen trioxide, nitrous acid, nitric acid and hydrogen peroxide. Most of the carbon monoxide and carbon dioxide in ambient air is emitted by combustion sources rather than by formation in atmospheric photochemical reactions. Sulfate and nitrate aerosols in ambient air also are formed in atmospheric photochemical reactions.

The organic vapors measured in the ambient air include a number of aldehydes including but not limited to formaldehyde, acetaldehyde and acrolein, along with methyl ethyl ketone, formic acid, peroxyacetyl nitrate and peroxypropionyl nitrate. A number of higher molecular weight complex organic substances have been identified in atmospheric aerosols. Based on comparisons with laboratory investigations, all of these substances are reasonably assigned as products of atmospheric photochemical reactions.

In the previous discussion, the assumption was made that products measured in simple systems in the laboratory also should be measurable in more complex laboratory systems and in the ambient air. Within the scientific review, the comparisons made do indicate satisfactory agreement in most instances between predicted and measured yields in experiments involving multicomponent hydrocarbon-nitrogen oxide systems. A number of products measurable as major products in individual simple and multicomponent hydrocarbon-nitrogen oxide laboratory systems also have been measured as products occurring at substantial loadings in the ambient atmosphere.

Finally, it should be noted that the biological effects of the products of atmospheric photochemical reactions are mentioned briefly but are not discussed in detail within the review. This aspect was not included as part of the effort requested.

Discussion of Issues

Three issues have been identified for consideration in this assessment. To provide answers to these issues requires use of both laboratory and ambient air measurements, because the ambient air measurements alone either are not complete or cannot be adequately interpreted at the present time.

Issue 1. Are the other products of atmospheric photochemical reactions, aside from nitrogen dioxide, present singly or in combination at significant ambient air concentrations compared to ozone?

As will be discussed in more detail below, several products do occur in the atmosphere at concentrations equal to 5, 10 or more percent of the ozone concentrations. These products are considered to occur at significant concentration levels compared to ozone. However, there also are a considerable number of products which occur individually at a few percent or less of the ozone concentration. Because of the large number of such products when summed they add up to significant atmospheric concentration levels.

The largest group of appropriate air quality measurements for making this evaluation has been obtained in California's South Coast Air Basin. The measurements made by long path Fourier transform infrared spectroscopy (LP-FTIR) are particularly useful. Such measurements were made at sites in Riverside, CA, Claremont, CA and Los Angeles, CA, during periods in 1977 through 1980. The LP-FTIR measurements provide ambient air concentrations of several products concurrently. This technique avoids possible sampling difficulties because of the open atmospheric path used.

Of the twenty-eight days of measurement available, twenty days were selected for the computations made because of the completeness and duration of the measurements obtained on those days. Concurrent measurements usually were available for ozone, formaldehyde, nitric acid, peroxyacetyl nitrate and formic acid. The lengths of the periods of measurement on these twenty days varied from six to twenty-three hours.

The percentages of other products in the ozone concentrations at the time of maximum ozone concentration will be considered first. Averaging the concentrations of each product at the time of maximum ozone concentration over the twenty days, the percentages of each of the other products in the ozone are as follows: formaldehyde, 11; nitric acid, 6; peroxyacetyl nitrate, 5; formic acid, 2. During several other air quality studies carried out in the South Coast Air Basin, formaldehyde, total aldehydes, or other individual aldehydes were measured. In these studies, the sum of the other aldehydes on the average about equalled the formaldehyde concentration. In some of the earlier studies made during the 1950's and 1960's, the total aldehyde concentrations were reported to equal or exceed the ozone concentrations.

Assuming that the sum of other aldehydes did equal the formaldehyde concentration during the LP-FTIR measurements, the total aldehydes would be about twenty-two percent of the ozone concentration during the more recent measurement period. This assumption is supported by the results of an independent study at one of the same sites within the 1977 to 1980 period.

Sulfates, nitrates, and secondary organic carbon aerosols also have been measured along with ozone in several other air quality studies within communities in the South Coast

Air Basin carried out between 1973 and 1979. Based on these results, the percentages of these aerosol products in the ozone concentrations at the time of maximum ozone concentrations are as follows: sulfates, 9; nitrates, 5; organic carbon, 4.

If these percentages for formaldehyde, other aldehydes, nitric acid, peroxyacetyl nitrate, formic acid, sulfates, particulate nitrates, and organic carbon aerosols are totalled, their sum is over half of the ozone concentration. If the earlier results for aldehydes were valid, these other products may have totalled a much larger percentage of the ozone concentration in earlier years.

The other products have diurnal concentration profiles differing from that of ozone. Therefore, the relationships between the other products and ozone on longer averaging time bases, such as 24-hour averages, will be different than at the time of maximum ozone concentration.

To explore the longer averaging time relationships, nine days were selected from the LP-FTIR measurement periods in 1977 to 1980. The products were measured for from ten to twenty-three hours a day during these nine days. Averaging the concentrations of each product over all of these measurement periods, the percentage each of the other products were of the ozone are as follows: formaldehyde, 31; nitric acid, 15; peroxyacetyl nitrate, 6; formic acid, 4. Again, the sum of other aldehydes will be taken as equal to formaldehyde based on other air qualities studies. The same studies of aerosol composition in the South Coast Air Basin discussed earlier also can be used to compute the percentages of the aerosol products in the ozone concentration on a 24-hour average. These percentages are as follows: sulfates, 15; nitrates, 11; organic carbon, 5. If these percentages, the formaldehyde, other aldehydes, nitric acid, peroxyacetyl nitrate, formic acid, sulfates, particulate nitrates and secondary organic aerosols are totalled, their sum exceeds the ozone concentration. There is about a two-to-one ratio between the percentage which these other products add up to on a longer time basis compared to the percent they sum to at the time of maximum ozone concentration.

In addition to the products discussed above, a number of other gaseous products have been measured in the South Coast Air Basin. However, the measurements for these products are not adequate to estimate their percentages of the ozone concentrations.

Similar air quality measurements are available for some of the products measured at urban locations elsewhere in the United States. The results are less complete than in the South Coast Air Basin. The only approach that appears feasible is to combine the measurements made at a number of locations such as in Houston, TX; St. Louis, MO; Columbus, OH; Atlanta, GA; and Hoboken, NJ. Even after combining results, the measurements are inadequate to estimate percentages at the time of maximum ozone concentration, but they can be used to obtain a diurnal basis. Based on this approach, the percentages the other products were of the ozone concentration on a 24-hour average basis are as follows: formaldehyde, 40; other aldehydes, 38; peroxyacetyl nitrate, 5; sulfate, 15. Since the percentages of these products sum to 98 percent of the ozone concentration, it seems reasonable to expect that the sum of all of the other products would somewhat exceed the ozone concentration on a 24-hour average.

Even fewer measurements are available at nonurban sites in the United States. Excepting sulfates, the concentrations of other products appear to be lower relative to ozone at nonurban than at urban locations.

The results discussed above indicate that the other products of atmospheric photochemical reactions can occur at significant concentration levels individually and at substantial concentrations in total compared to ozone. Additional health and welfare research results are needed to adequately evaluate the significance of these air quality results to criteria and standards development.

Issue 2. Can ozone through its air quality measurements be used as a surrogate for the other products observed in the ambient atmosphere?

It is important to decide what the term "surrogate" means in the context of this issue. Two possible viewpoints are suggested here. Firstly, the term surrogate can be interpreted to mean that other products display the same directional characteristics as ozone. Secondly, the term surrogate can be interpreted to mean that unique quantitative relationships exist between ozone and other products. Both possibilities will be considered here. Two approaches are available. One of these examines the relationships that occur in laboratory studies between hydrocarbons and nitrogen oxides precursors and the photochemical reaction products. The second approach examines the possible relationships indicated by concurrent measurements in the ambient atmosphere of ozone compared to other products.

The laboratory results used are from three different smog chamber irradiation studies. Measurements are available from these studies for oxidant or ozone along with peroxyacetyl nitrate and/or formaldehyde. The results obtained were expressed either as concentrations of products or dosages (concentration x irradiation time) of products.

The experimental designs were such that three precursor-product conditions were investigated: (1) the initial hydrocarbon was varied (from experiment to experiment) over a range of concentrations with the initial nitrogen oxide at a fixed concentration, (2) both the initial hydrocarbon and the nitrogen oxide concentrations were varied but with a constant ratio of these precursors, and (3) the initial nitrogen oxide was varied over a range of concentrations with the initial hydrocarbon at a fixed concentration.

The conclusions that can be obtained from the experimental results relevant to the three conditions listed above are as follows:

Condition 1. The concentrations and the dosages of products vary in the same direction with changes in the initial hydrocarbon concentration. The amounts of variation of any one product with the changes in initial hydrocarbon concentration are different from any other product.

Condition 2. The concentrations and dosages of products under many experimental circumstances vary in the same direction with the concurrent changes in initial hydrocarbon and nitrogen oxide concentrations. At lower precursor ratios, the concentrations and dosages of other products can decrease while the oxidant increases. The amounts of variation of any one product with the concurrent changes in initial hydrocarbon and nitrogen oxide concentration are different from any other product.

Condition 3. The concentrations and dosages of products under many experimental circumstances vary in the same direction with the changes in initial nitrogen oxide concentrations. In two of the three studies, the concentrations of one of the other products did not vary in the same direction as the oxidant or ozone with the changes in initial nitrogen oxide concentrations. The amounts of variation of any one product with the changes in initial nitrogen oxide concentration are different from any other product.

These laboratory results indicate that other products under many, but not all experimental circumstances, will vary in the same direction as the oxidant or ozone with changes in the concentration of precursors. The quantitative variations in other products are not the same as for oxidant or ozone with changes in the concentration of precursors.

In the second approach used, the ambient air relationships were examined between ozone and several other products. The measurements available by long path Fourier transform infrared spectroscopy at several locations in the Los Angeles Basin were used. In these ambient studies, precursor concentrations are only occasionally reported. Since neither precursor emissions nor ambient air concentrations upwind are reported in these studies, it is not possible to relate products to precursors from these studies. However, ozone concentration distributions can be compared with those for peroxyacetyl nitrate, nitric acid, formaldehyde and formic acid.

The results for maximum diurnal ozone concentrations were plotted relative to the concentrations at the same times for each of the other products. Results obtained at University of California, Riverside, CA in 1976 and 1977; at Harvey Mudd College, Claremont, CA in 1978 and 1979; and at California State College, Los Angeles, CA in 1980 were used. The conclusions which can be arrived at by examining such plots are as follows:

(a) The concentrations of other products show the same directional characteristics as the ozone concentration.
(b) These relationships are not linear. Significant curvatures are apparent in the plots, particularly at the higher concentrations measured. Corresponding to a fifty percent reduction in the concentration of ozone from its highest measured diurnal maximum concentration, the concentrations of the other products decreased by more than 50 percent.
(c) There is considerable scatter in the measurement values of each of the other products at a particular ozone concentration. For example, in the 270-280 ppb range of concentration for ozone, the formaldehyde concentrations ranged from 12 ppb to 31 ppb.
(d) The scatter in measured values is not random. Based on the ozone-formaldehyde plot in the 200-300 ppb ozone range, the lowest concentration values of formaldehyde were reported at Riverside, CA in 1976 while those in Claremont, CA in 1978 are consistently high with the results of the other two studies at these locations falling in between these studies. Similar site-specific effects can be identified in the other plots.
(e) The amount of scatter varied from plot-to-plot. The results for the ozone-peroxyacetyl nitrate plot show the least scatter. The variability observed is likely to be due to a combination of factors including differing effects of transport, varying contributions of local primary emissions of products to the total loading of products, and differences in precursor emission densities.

These ambient air results suggest that at least in the South Coast Air Basin ozone serves as a surrogate directionally for other products. Adequate measurements are not available in other geographical areas relating ozone to a number of other products.

Issue 3. Is it possible to conduct ambient air monitoring for photochemical reaction products other than ozone?

Satisfactory "routine" monitoring techniques for other products are needed if a separate standard should be considered for products other than ozone.

Most of the results available are from research studies of short duration. However, several monitoring efforts have been carried out for other products. Both the Los Angeles Air Pollution Control District during the 1950's, and the state of New Jersey during the 1970's, monitored aldehydes or formaldehyde. Automated gas chromatographic equipment has been utilized in Riverside, CA to obtain several years of peroxyacetyl nitrate measurements. Therefore, measurements for several products appear to be possible on a routine basis. The available results indicate that it should be possible, if desired, to conduct a monitoring effort at least in a limited number of critical urban areas.

Conclusions and Recommendations

1. Other gaseous and aerosol products of atmospheric photochemical reactions in combination occur at substantial concentration levels in the ambient air compared to ozone in urban areas. On a 24-hour average basis, these other products in combination can equal or exceed the ozone concentration. At the time of maximum ozone concentrations, the other products can constitute in combination about half of the ozone concentration. Based on incomplete carbon and nitrogen balances obtained in laboratory measurements,

additional laboratory and field studies are needed to complete the identification of products.

2. Ozone may serve as a satisfactory surrogate directionally for other products in the ambient atmosphere. Although the other products show similar qualitative variations in the atmosphere as ozone, quantitative relationships are much more complex. Laboratory studies relating oxidant, formaldehyde and peroxyacetyl nitrate to precursor concentrations indicate somewhat different relationships for each product.
3. In view of concern from the air-quality viewpoint for the other products, additional clinical and epidemiological health studies are needed. If any of the other products should prove to have a dose-response curve comparable to ozone, that other product might be included in a standard by either developing an "equivalent" ozone standard or estimating a margin of safety. By "equivalent" ozone standard is meant a standard in which the impact of the concentrations of other products would be adjusted by equating them to particular concentrations of ozone.
4. It appears practical to carry out monitoring efforts for other products than ozone, if necessary, in a limited number of critical urban areas.

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